Pergamon

Cement and Concrete Research 31 (2001) 941–947

CEMENT AND CONCRETE RESEARCH

Possibilities of the use of isoperibolic calorimetry for assessing the hydration behavior of cementitious systems

J. Brandštetr*, J. Polcer, J. Krátký, R. Holešinský, J. Havlica

Institute of Materials Chemistry, Faculty of Chemistry, Technical University, Purkyňova 118, 61200 Brno, Czech Republic

Received 4 December 2000; accepted 16 February 2001

Abstract

The possibilities of a new multicell isoperibolic–semiadiabatic calorimeter for the measurement of the hydration heat evolution of binders in pastes, mortars and concretes of different composition during setting and early hardening are presented. Up to 32 samples can be tested simultaneously. The measurements enable to study the influence of the main constituents as well as minor organic and inorganic additives on hydration, to estimate the start of setting and to calculate the partial heat of hydration during a given time of curing. Due to the simple construction, no special service is demanded. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calorimetry; Concrete; Cement; Hydration; Admixture

1. Introduction

The common property of binders is their exothermic reaction with water, the hydration heat value being the characteristic feature of each binder in question. The values measured are integral heats covering all the reactions running in setting and hardening pastes (mixtures): heat of wetting, heat of solution of individual constituents, hydration of ions being transferred into the solution, heat of precipitation or crystallization, reactions of new hydrates formed in the mixture, etc. In spite of this multiplicity, calorimetry provides data indispensable in characterizing the chemical behavior of cement, lime and other binders especially in their mixtures with different constituents [1–7]. The values of hydration heats of individual clinker minerals represent the fundamental data in the thermochemistry of clinkers and cements. The effect of many main constituents of binders, such as slags, fly ashes, silica fumes, pozzolans, etc. and minor additives (retarders, accelerators, superplasticizers) studied by calorimetry contribute to the optimization of the composition of mortars and concretes produced from different, often unusual raw materials, allowing the preparation of "tailored" composites according to the demand of the user. Interesting results were obtained by measurement of progressive noncement mixtures of blast furnace slag activated by alkali compounds [8]. At present, calorimetric measurements evaluating the effect of superplasticizers (SP) are of fundamental importance. Their compatibility with the cement in question is being studied insufficiently and mostly neglected [9–11]. Very important is the possibility of estimating the start of setting, which coincides with the beginning of hydration determined by calorimetric measurement.

The calorimeters proposed for the measurements of hydration heat are based on very different principles, some of them are available on the market and used at present more preferably in the research laboratories [1,3,6,7]. Thermochemistry of silicates and calorimetry became an important part of many branches of industrial activities.

2. Heat of hydration as determined by calorimetric methods

According to new European standards, two calorimetric methods for the determination of hydration heat of cement were introduced to monitor the chemical and phase composition as well as the fineness of the 25 different kinds of cements according to EN 197-1.

---

* Corresponding author. Tel.: +420-5-41149365; fax: +420-5-43211101.

E-mail address: brandstetr@fch.vutbr.cz (J. Brandštetr).

PII: S0008-8846(01)00495-1

The solution methods according to EN 196-8 and the ASTM C 186 standard test solution method for heat of hydration of hydraulic cement are based on the measurement of the dry cement dissolution heat in the mixture of acids and the heat of dissolution of a separate portion of the cement that has been partially hydrated for 7 and for 28 days, the difference between these values being the heat of hydration for the respective hydrating period. A certain disadvantage of this method is its low accuracy due to the final value representing small difference between two large values and the necessity of waiting on the results 7 or 28 days, respectively.

The semiadiabatic method (EN 196-9) is based on the determination of the emitted heat by measuring the temperature development of the freshly made sample to a given time point during setting and hardening. This direct method is more favored and more indicatory because the curves show the course of reactions running immediately after mixing the components under given conditions.

The calorimeters used in this kind of testing are constructed as adiabatic (preventing the heat exchange with the surroundings) or semiadiabatic, isoperibol or isothermal (at constant temperature of the environment) and conductive (measuring the rate of heat evolution from the temperature gradient between the sample and the metal envelope of constant temperature). Each of these methods has its advantages and supplies specific data describing individual perspectives on the rate of hydration under different ambient temperature and curing conditions.

3. Multicell isoperibolic calorimeter

To enable a simultaneous measurement of a series of samples, a multicell computerized calorimeter measuring in isoperibolic or semiadiabatic mode was constructed in our laboratory [1]. The 200 ml Styrofoam reaction beakers (1.6 g of weight) with the proper amount of sample (usually 300 g) are placed in a thermoinsulating envelope, in the thermostat or free in the laboratory. The surface of the fresh sample is covered with a paraffin oil layer to prevent evaporation of water. For testing of concrete mixes, heavier samples can be used. The temperatures of the samples are measured by means of thermocouples in thin steel envelope connected with the interface card built in the computer, which records the temperatures of the individual samples at given intervals. One sensor is situated free near to the calorimeter to monitor the temperature in the laboratory.

The calorimeter enables not only the testing of the reactivity of cements, but — more important — it may be used to measure the rate of reactions in mixes (pastes, mortars, concretes) of different composition, including noncement composites, by monitoring the effect of different main constituents of binders, the influence of the kind and amount of organic or inorganic minor admixtures, the influence of w/c ratio, the starting temperature, etc. on the course of hydration. This kind of measurement also enables to estimate the start of setting and to calculate the value of partial hydration heat of the binders for a given period. The instrument also enables to characterize the quality of quicklime, i.e., the content of available lime and its hydration rate [1].

An essential part of the multicell calorimeter is the thermoinsulating envelope which prevents the heat exchange between the hydrating sample and the surrounding to a great extent. The adiabatic calorimetry simulates the behavior of the hardening concrete inside a massive block, whereas the isoperibolic measurement performed without any insulation of the beaker reflects the conditions on the periphery of the block. The large temperature difference, which may develop, may cause undesirable cracks and loss of strength, limiting thus the use of ordinary portland cements possessing higher hydration heat.

In Fig. 1, the influence of different insulating envelope, as well as the role of an oil layer on the surface of the sample, is presented.

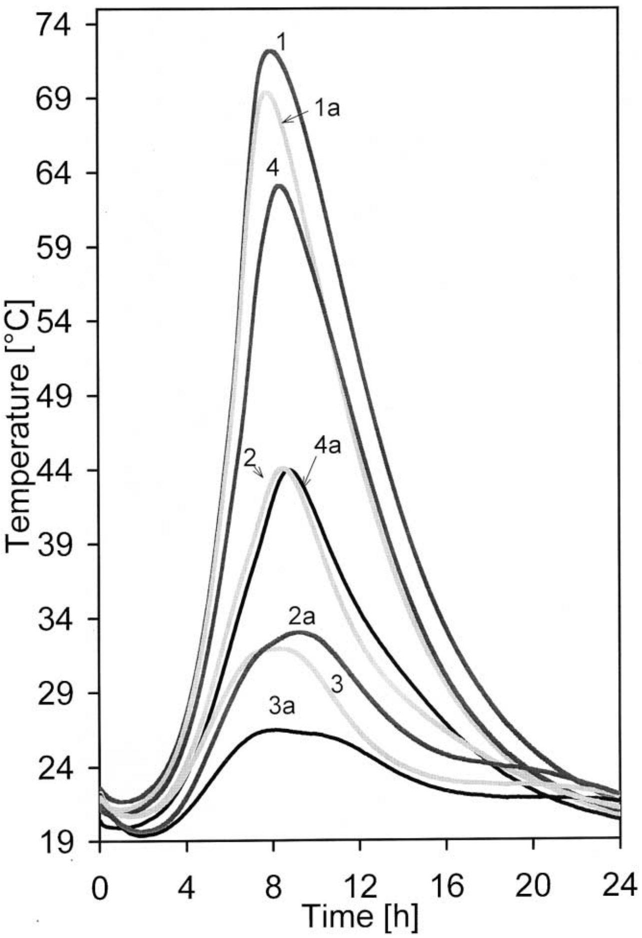

Fig. 1. The course of hydration of portland cement CEM I 42.5 paste, w/c = 0.30, at different thermoinsulation of the reaction beaker (300 g of sample). (1) Styrofoam block, oil layer. (1a) Ditto, without oil. (2) Polyurethane cylinder, oil layer. (2a) Ditto, without oil. (3) Free in the thermostated laboratory, oil layer. (3a) Ditto, without oil. (4) 200 g of the sample, oil layer. (4a) 100 g, ditto.

The Styrofoam block (5 cm of wall thickness, including the cover) produces the best insulation. The effectivity of the oil layer is illustrated by the curves 1, 1a (2, 2a) on Fig. 1. The lowering of the weight of the sample from 300 g to 200 or 100 g, respectively, results in decreased thermal peaks (4, 4a). In the case of greater samples, the higher temperature reached by the hydration heat accelerates the process of setting and hardening. On the contrary, the use of very small samples without a thermoinsulation enables to distinguish individual reaction peaks, which at higher peak would merge and could not be distinguished. The measurements are limited by the boiling point of water, therefore, some rapidly reactive binders exhibiting high heat of hydration must be diluted by an inert substance (coarse sand) or the measurement must be performed in a reasonably weaker thermoinsulation. The calorimeter should be situated in a shaded laboratory at constant temperature, usually within 22.5–23.5°C, which is monitored by one thermoelement placed free near the calorimeter. The important advantage of this calorimeter is its very simple construction which necessitates no special service. The heart of the instrument is the measuring card connecting the thermocouples with the computer.

The PC program must meet particular demands on the exact measurements of diverse samples simultaneously up to 32, mostly, 8 samples are convenient and sufficient. The program is arranged for the operational system DOS using two-step cascade filtration of measured values to avoid random and synchronous interferences. It is possible to begin each individual measurement at the optional time, independently of other samples; similarly, each measurement can be stopped separately. Series of samples must be prepared in the same way, usually successively in a standard mixer. Each mixture is weighed into the Styrofoam beaker, the portion is compacted by tapping, 5 ml of paraffin oil is poured on the surface and, after the thermoelement is inserted, the measurement may be started. To protect the thermosensors from corroding in strong alkaline media, it is best to place them into a thin plastic envelope. On the monitor, the following data are displayed and stored into a table:

- number of the sample (beaker),
- kind of the sample,
- actual temperature of the sample at a given moment, and
- time elapsed from the start of measurement.

The temperatures of individual samples are monitored each 3 s. First interval (for fast reactions) is 0–12 min, then it is automatically prolonged to 0–24 min, 60 min, 2 h, 8 h, 24 h, 5 days. The scale on the monitor is automatically changed adequately, enabling to follow the course of the reaction curves. The rate of cooling, which may be different according to the thermoinsulating envelope employed, can be calculated from the monitored temperatures and serves as a basis for the calculation of the partial hydration heat of the tested cement (binder) within a given interval of curing.

4. The influence of the main constituents ratio on the heat of hydration

At present, the production of cements containing different kinds and amounts of cementitious constituents (EN 197-1, Types II–V) is increasing, which saves mineral resources, enables the use of industrial by-products and reduces carbon dioxide emissions. Very often, low heat of hydration is demanded. In using mineral raw materials of different origin, composition and grain size, the tests of reactivity by a proper calorimetric method as well as the strength activity index determination (EN 450) are of fundamental importance. As an example, portland slag cements (II/A-S and II/B-S) and blast furnace cements (III/A,B,C), which differ in their clinker-to-slag ratio were tested. The pertinent calorimetric curves are presented in Fig. 2. As expected, the increasing amount of BFS decreases

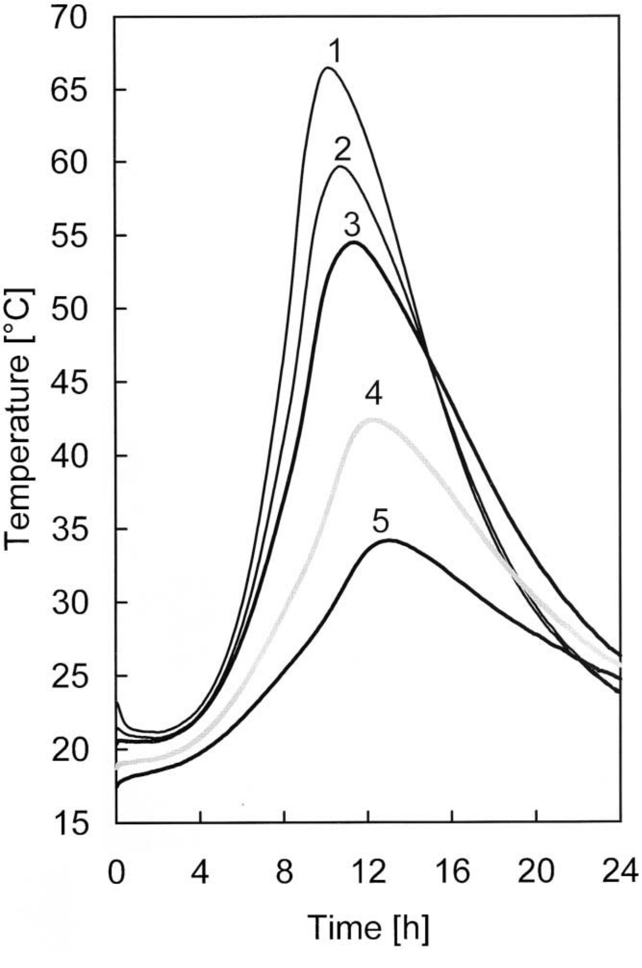

Fig. 2. Rate of hydration of portland cements with different amount of GBF slag, w/c = 0.30 (300 g of paste, measured in Styrofoam block). (1) CEM I 42.5. (2) CEM II/A-S (15% of GBFS). (3) CEM II/B-S (35% of GBFS). (4) CEM III/A (55% GBFS). (5) CEM III/C (85% GBFS).

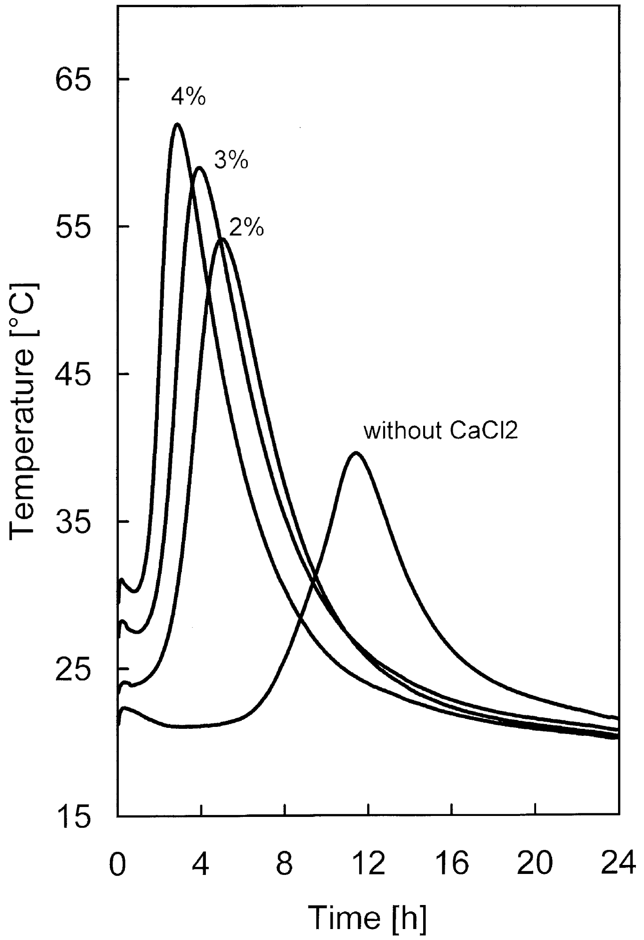

Fig. 3. Effect of calcium chloride on setting of portland cement CEM I 42.5 diluted with sand 2:1, w/c = 0.30, $CaCl_2$ in % on PC (300 g of paste, measured in polyurethane cylinder).

the hydration heat of the cement in question and slightly retards the setting, which starts with the beginning of the main hydration period.

5. The effect of calcium chloride as an accelerator of setting

The most used accelerating admixtures are soluble calcium salts, especially cheap calcium chloride. Its effect is evident even at low concentrations (Fig. 3).

6. Effect of SPs, compatibility with cements

Increasing demand for high performance concretes, self-leveling pumpable concretes, self-compacting concretes and shotcretes directs the producers of chemical admixtures to develop still more efficient SPs allowing to maintain the proper consistency of the fresh mortar and concrete at low water-to-cement ratios during the time of their placement. The molecules of water-soluble polymer react at the cement–liquid phase interface, changing the charge of the cement particles, as may be seen in the measurement of the zeta-potential. Individual clinker minerals possess different reactivity with a given chemical admixture. In the presence of a SP, the degree of particle aggregation in the paste becomes reduced, thus altering the progress of setting and hardening and improving the bond between cement matrix and aggregate. Many constituents in cements exhibiting a certain hydraulic and/or pozzolanic reactivity also consume a part of the SP added, but considerably less than C_3A in portland cement or CA in aluminate cement. The effect of the SPs in such cement pastes or composites can be tested parallel with the measurement of the consistency, e.g., by the flow table test, by measuring the slump, by the Marsh cone method, by penetration test (Vicat) or by rheometers.

The increasing number of SPs of different chemical composition available as well as the high number of cements of different types makes the situation complicated. Last but not least, the effect of grinding aid cannot be neglected. The activity of the salesmen and lack of professional information on the proper use of these individual modification agents often leads to neglecting the compatibility of the reacting constituents, the R&D and proper recommendations are urgently needed. The use of calorimetry complementing other tests of the properties of the fresh paste and consequently of the hardened mortars or concretes seems to be indispensable.

SPs can be divided into four fundamental types [9] according to their chemical constitution. Many of them are sulfonates reacting preferably with tricalcium aluminate in cement, which competes with the retarding action of calcium sulfate. The influence of the basic part of the molecule of the SP as well as the average molecular weight determines the properties and utilization of SP [9].

The first plasticizers used in concretes were lignosulfonates produced from the by-products of paper mills. Other types of SPs are based on sulfonated naphthalene or sulfonated melamine condensates with formaldehyde. At present, a new generation of SPs containing carboxylic functional groups is being introduced, which disperse cements at lower concentrations. Polymers based on polyacrylates are less common.

A series of calorimetric measurements with different SPs and cements were performed, curves of some of these experiments are presented. The proper dosing of the admixture is very important, the surplus usually brings about retarding effect and decreases the strengths. The curves enable to assess the effectivity of the SP and its compatibility with a given cement, but the last final answer can give only direct laboratory tests.

The curves indicate the distinct effect of Peramin V on the hydration process even at low concentrations 0.2–0.5%. The admixture exhibits a rather strong retarding effect, the high concentrations may prevent the hydration completely. The first peak on the curves is brought about by the adsorption of SP on the surface of the cement grains and increases with the concentration of the SP (Fig. 4).

The rate of hydration of cements CEM II–V with different mineral main constituents may differ depending on their hydraulic and/or pozzolanic reactivity.

In portland-slag cement, the first exothermic peaks are more expressive in comparison with those in CEM I pastes due to a reduced reactivity of BF slag. Thus, the clinker minerals are here oversuperplasticized (Fig. 5).

The effect of melamine-based SP was less pronounced. Increased amounts showed a gradual extension of the induction period, but no retardation in the development of the main exothermic peak which became enhanced (Fig. 6).

An important advantage of calorimetric measurement is the possibility to estimate the start of setting.

The consistency was measured by the Vicat needle penetration test in an automatic device. The start of setting given by Vicat test coincided with the start of the evolution of the hydration heat after the dormant period (Fig. 7). The intensive first reaction peak immediately after the addition of water with SP indicates a reaction of the SP with the cement in question, depending on the content and quality of calcium sulfate present.

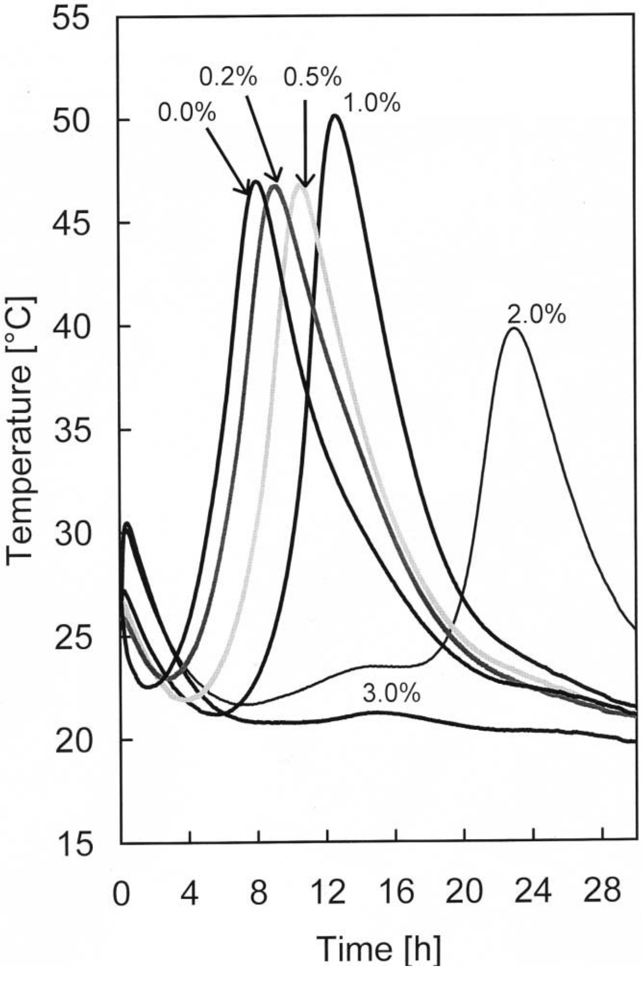

Fig. 4. The influence of increasing amount of lignosulfonate type SP on the course of hydration heat evolution of the CEM I 42.5 (w/c = 0.33, SP Peramin V was added together with water, 300 g of paste, measured in the polyurethane cylinder).

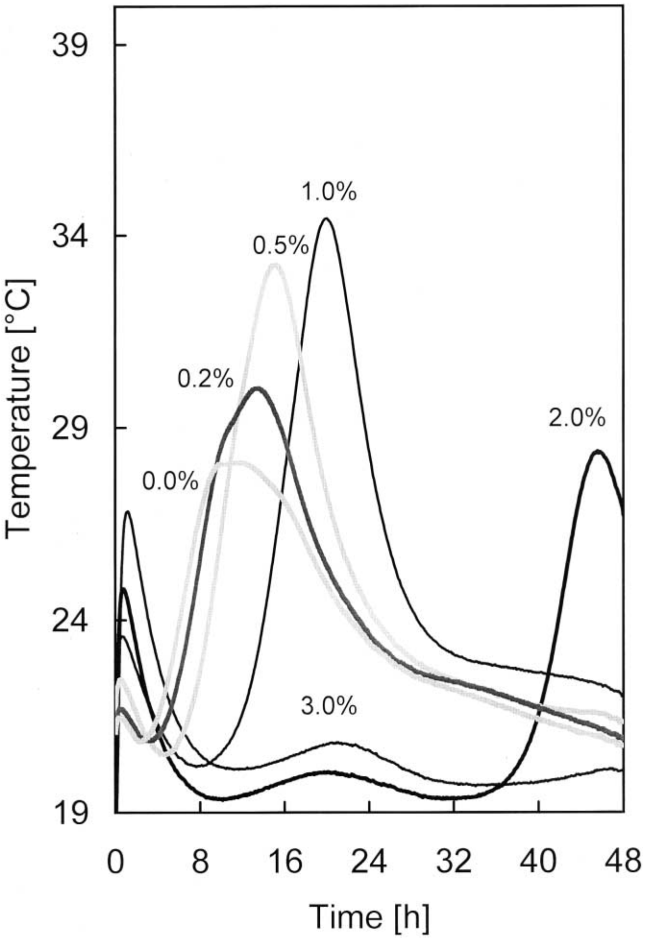

Fig. 5. The influence of increasing amount of lignosulfonate type SP on the course of hydration heat evolution of portland slag cement CEM II/B-S 32.5 (300 g paste, w/c = 0.33, SP Peramin V was added together with water, measured in polyurethane cylinder).

Using the same mixtures, the effect of increasing amount of SP on the compressive strengths of the pastes was measured after 1, 15 and 28 days, respectively. The tests on moist-cured specimens 20 × 20 × 100 mm (Fig. 8) indicate the effectivity of this SP even at low concentrations, 0.2% is often a sufficient amount, producing good consistency and strengths.

7. Conclusions and comments for further research

The need for rapid quality tests of binders and especially of fresh mixtures of mortars and concretes of different chemical and phase composition led to the construction of computerized multicell isoperibolic (semiadiabatic) calorimeter enabling measurement of up to 32 samples simultaneously, a series of 8 samples are usually sufficient. The

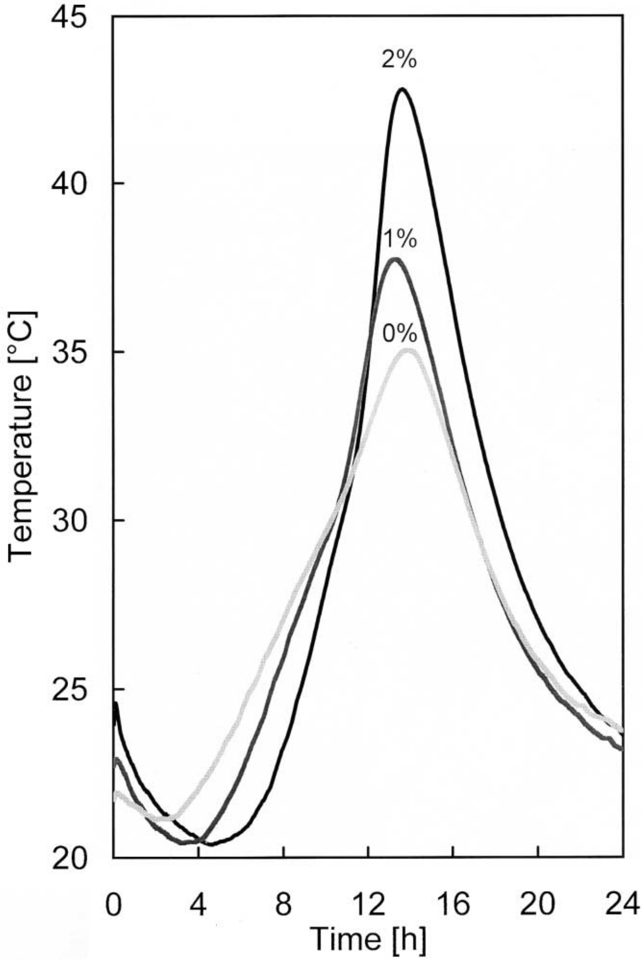

Fig. 6. The influence of melamine type SP on the course of hydration heat evolution of CEM I 42.5 (w/c = 0.33, SP Peramin F, 300 g of sample measured in polyurethane cylinder).

possibility of performing a series of measurements under the same conditions enable to get a great number of results in a short time characterizing the tested binders and mixtures. The simple construction does not need service and repair, the main part of this instrument is the interface measuring card for the connection of the thermosensors to the PC and the program.

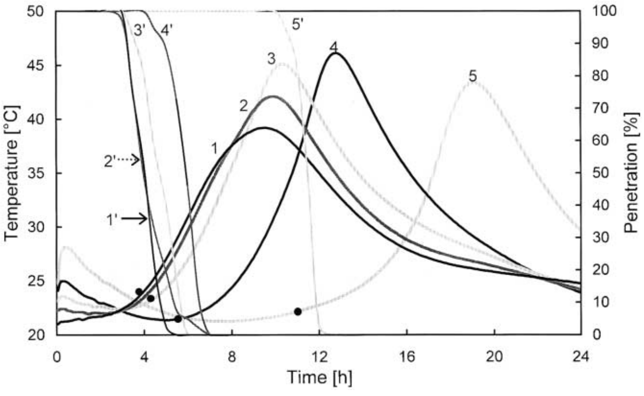

Fig. 7. The estimation of start of setting of CEM I 42.5 from the calorimetric and penetration curves measurement (w/c = 0.33, SP Sikament Multimix 100, 300 g of paste, measured in polyurethane cylinder).

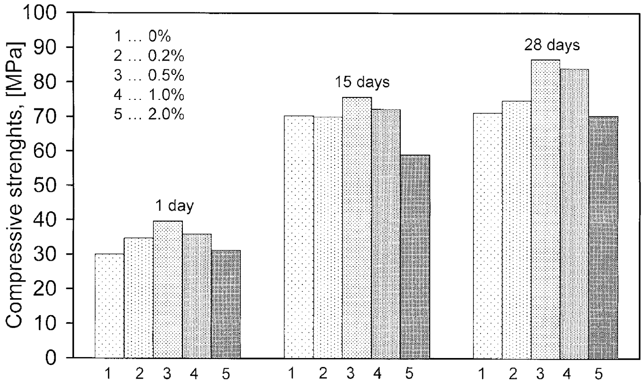

Fig. 8. Compressive strengths of CEM I 42,5 paste specimens with increasing amount of SP Sikament Multimix 100 (Conditions: see Fig. 7).

On examples, the usefulness of this calorimeter for testing the quality of cements, the reactivity and effectivity of the main mineral constituents (slag, fly ash) and of different modifying chemical admixtures (accelerators, SPs) in pastes or mortars is demonstrated. The measuring of the course of reactions in fresh setting mixtures enables the optimization of the composition of the mixture, thus producing "tailored" high performance composites. It should be commented that the same type of cement, but produced by different cement works, can possess different phase compositions and thus exhibit different reactions with the tested SP (compatibility). Each measurement makes it possible to estimate the start of setting, which coincides with the beginning of the exothermic reaction of hydration after the dormant period. The special program enables to calculate the partial hydration heats within the given period.

Specialized demands often need economically available instrumental techniques. The possibility of performing a series of calorimetric measurements under the same conditions enable to get a large number of results in a short time and to present more accurate data illustrating the possibilities of new admixtures and composites, complementing results obtained by other methods.

At present, SPs are indispensable admixtures, especially for the production of high performance and high strength concretes. The utilization of these soluble polymers offered in a wide assortment often lacks sufficient information on their compatibility with the individual types of cement, which may be a problem of the cement works. The main role is played by the mineralogical composition of the clinker (especially the content of calcium aluminates) and the amount and quality of the calcium sulfate of different origin and composition. The estimation and improvement of the compatibility is a task for the research of the producers of SP, who are still introducing new SP (e.g., based on cross-linked copolymers) to enhance their reactivity, which allows to lower the concentration necessary for the demanded effect.

It is necessary to comment that SP very often cause retardation of setting, which is perfectly demonstrated by calorimetric curves. The effect of some minor constituents (e.g., phosphates, heavy metals) has been poorly studied so far, due to the great number of needed experiments.

The scope of this paper is not to present rules estimating the compatibility of SP with the type of the given cement. The complexity of the problem needs individual approaches evaluating a great number of laboratory experiments, which can be reliably performed on the new multicell calorimeter presented. At present, calorimetric measurements become indispensable supplements for the successful research in the silicate chemistry and technology of building materials.

References

[1] J. Brandštetr, J. Polcer, Eight-cell isoperibolic calorimeter for measurement of hydration heats of cements and other systems, Fly Ash, Silica Fume, Slag Nat. Pozzolans in Concr., Proc. Int. Conf., 6th, CANMET/ACI, Bangkok, 1998, 527–537 (Supplementary papers).

[2] L.D. Adams, The measurement of very early hydration reaction of portland cement clinker by thermometric conduction calorimeter, Cem. Concr. Res. 6 (1976) 293–308.

[3] J. Brandštetr, Adiabatic calorimeter for the measurement of the rate of hydration of binders in the mixtures of different composition, (in Czech), Silika 4 (1994) 31–34.

[4] R.I.A. Malek, Methods of performing adiabatic and isothermal calorimetry, Proc. 9th International Congress for the Chemistry of Cement, vol. VI, New Delhi, 1992, pp. 210–215.

[5] V. Ambrúz, J. Havlica, J. Gabrišová, Use of differential calorimetry for characterization of hydration processes, J. Thermal. Anal. 33 (1988) 647–650.

[6] RILEM TCE 1: Adiabatic and semi-adiabatic calorimetry to determine the temperature increase in concrete due to hydration heat of the cement, Mater. Struct. 30 (1997) 451–457.

[7] A. Usherov-Marshak, Calorimetric analysis in the chemistry of cement, Proc. 10th International Congress for the Chemistry of Cement, vol. III, Gothenburg 1997, p. 8 (paper 016).

[8] E. Douglas, J. Brandstetr, A preliminary study on the alkali activation of ground granulated blast-furnace slags, Cem. Concr. Res. 20 (1990) 746–756.

[9] V.S. Ramachandran, V.M. Malhotra, C. Jolicoeur, N. Spiratos, Superplasticizers: Properties and applications in concrete, CANMET, Ottawa, 1998, p. 404.

[10] P.-C. Aitcin, High-Performance Concrete, E & FN Spon, New York, 1998, p. 591.

[11] A.A. Ramezanianpour, V. Sivasundaram, V.M. Malhotra, Superplasticizers: Their effect on the strengths properties of concretes made with ASTM type I and V cements, Superplast. Other Admixtures Concr., Proc., Int. Conf., 4th, CANMET/ACI, Ottawa, 101–126 (Supplementary papers).